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Immobilised heteropolyacids in zirconia and silica matrix by sol gel and wet impregnation techniques for glycerol acetylation

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Abstract
This work focuses on the synthesis, characterisation and catalytic activity of heteropolyacids immobilised in zirconia and silica. The principal aims of this study are: (i) to compare the catalytic activity of pure heteropolyacids (HPA) in the glycerol acetylation carried out with an excess of glycerol; (ii) to immobilise the most active HPA in two different supports, zirconia and silica, by two different methods (wet impregnation and sol-gel technique); (iii) to compare the properties of the final solids, depending on the matrix and the synthesis method used; and finally (iv) to test these solids in the glycerol acetylation carried out in an excess of glycerol. Nitrogen adsorption desorption, XRD, ICP-AES and FTIR techniques were used to characterise the samples. Zirconia samples exhibited low surface area and silica solids presented micro and mesoporous textures. Both matrixes were amorphous. Wet impregnation method resulted in crystal formation of HPA which were completely soluble in polar media. Sol-gel samples showed a very high immobilisation yield but did not show good performances in catalytic test. Keggin HPA unit was preserved all over the preparation of the solids, and presented some geometrical distortion possibly due to a strong interaction with the matrix. This interaction could induce a modification of the acidic properties which could explain the absence of catalytic activity during the esterification test.

Keywords: *Acetic acid, biodiesel, esterification, glycerol, heteropolyacids.*

Introduction

Keggin heteropolycompounds are well defined structures formed by a polyanion $[XM_{12}O_{40}]$ and a cation. This work is focused on Keggin heteropolyacids (HPA) where the cation is a proton H^+. The HPA are used as acid catalysts, due to their strong Brönsted acidity in presence of water [1]. The structure of the HPA and the different elements participating in their formulation determine the solid properties as the chemical and thermal stability and their acidity. Taking into account the acid strength, Keggin type heteropolyacids can be ranked from the most acidic to the lest acidic as follows: $H_3PW_{12}O_{40}$, (HPW)>; $H_4SiW_{12}O_{40}$, (HSiW)> $H_3P_2Mo_{12}O_{40}$ (HPMo) >$H_4SiMo_{12}O_{40}$ (HSiMo). HPA are soluble in polar solvents, so they can be used in esterification reactions as an alternative of H_2SO_4, as they are less toxic, volatile, corrosive and more active than conventional mineral acids [2]. The immobilisation of HPA results in an increase of the surface area and facilitates the recovery process which makes them suitable for heterogeneous catalysis avoiding contamination of final products, corrosion of the equipment and low recyclability. When wet impregnation method is used, zirconium hydroxide is the most common support as it offers a stronger interaction between the solid and the HPA compared to silica [3]. This phenomenon is due to a large amount of hydroxyl groups which are capable of stabilising the HPA on the surface of the zirconia [4]. When sol-gel technique is used, the HPA is incorporated generally in a silica matrix, even if several works have studied also the titanium and the zirconia as matrix [5-8]. This method provides a better immobilisation of the HPA than wet impregnation technique. HPA supported on zirconium hydroxide are suitable, active and recyclable solids for the esterification reaction between primary alcohols n-butanol and iso-butanol and formic, acetic and propenoic acid and also secondary alcohols, cyclohexanol and iso-butanol and acetic acid [4, 9]. Concerning the glycerol acetylation in presence of a large excess of acetic acid, Ferreira and co-workers has successfully performed catalytic

reactions over molybdophosphoric acid immobilised in USY zeolites [10] and tungstophosphoric acid immobilised on silica catalysed [11].

However there is a lack of studies comparing the performances of immobilised HPA in different matrixes. In this work two synthesis methods are used (wet impregnation and sol-gel) with two different supports: zirconia and silica.

Experimental

The HPW immobilised in zirconia were prepared by one-step sol–gel technique by hydrolysis of zirconium (IV) propoxide (70% in propanol, Aldrich) with distilled water. After stirring the mixture (1mol Zr/l propanol) for 90 min at 313 K under nitrogen atmosphere) the heteropolyacid dissolved in a mixture of distilled water and propanol (50% vv) was added slowly. The amount of water was fixed in order to reach a molar ratio of hydrolysis H_2O/ZrO_2 equal to 1. The gel obtained was aged 5 days and then dried at 353 K under vacuum. The resulting powder was divided into different fractions which underwent different treatments: calcination in air for 3 h at 473 K or Soxhlet extraction with distilled water for 24 hours at approximately 343 K.

The HPW encapsulated in silica were synthesised by the sol–gel technique proposed by Izumi and co-workers with some modifications. A mixture of water (2.0mol), ethanol (0.2mol) and heteropolyacid was added slowly to tetraethyl orthosilicate (0.2 mol) at 353 K under nitrogen atmosphere. After gelation, the mixture was dried at 353 K under vacuum. A fraction of the resulting powder was washed with distilled water for 24 h with a Soxhlet apparatus at approximately 343 K.

Zirconia and silica solids were prepared without adding HPW, and used as supports for the wet impregnation technique. For samples obtained by wet impregnation method (WI), the support was suspended in distilled water in which a quantity of HPW was dissolved (1 g support/ 50 ml of water). The mixture was stirred for 2h, and then water was eliminated by vacuum drying in a rotary evaporator. The resulting powder is dried in an oven 393 K overnight. A fraction of the solid obtained was calcined at 473 K in air for 3 h. Soxhlet extraction with distilled water and at approximately 343 K was also applied.

Sol-gel samples were named as: Nn-PW-loading %wt-tt-S, where «Nn» is the matrix (Zr for zirconia and Si for silica), «ht» is the thermal treatment applied (D for dried samples at 353 K and 200 for calcined samples at 473 K) and «S» stands for Soxhlet extraction. For wet impregnation samples «WI» is added: Nn-PW-loading %wt-WI-tt-S.

The catalysts are characterized by nitrogen adsorption, XRD, ICP-AES and FTIR.

The esterification reactions were carried out at 328 K and atmospheric pressure in a round bottom flask reactor equipped with a magnetic stirrer and placed in an oil bath. The acetic acid (puriss. p.a., ACS reagent, ≥99.8%, GC/T, Fluka) concentration was 100 g/l of glycerol (puriss. p.a., ACS reagent, anhydrous, dist., ≥99.5%, Fluka) which corresponds to an initial molar ratio acetic acid: glycerol = 1:8; the catalyst concentration being 6.25 g / l of glycerol. Samples of the reaction medium were analysed by gas chromatography (Cp-Sil 8CB column with a FID detector), after extraction with 1-heptanol (98 %, Sigma Aldrich) using o-xylene (98 %, Aldrich) as the internal standard. The activity results are presented in terms of total yield of esters obtained and conversion of acetic acid.

In comparison, pure HPA were used for homogeneous catalysed reactions HPW, HSiW, HPMo and HSiMo.

The test procedure was as follows: the catalyst was put in the reactor together with the glycerol and the mixture was brought to the reaction temperature. When the temperature was reached, acetic acid was injected. One minute after the injection, a sample was taken and analysed. This result was considered as the initial chemical composition of the medium. This process was necessary to exclude the possibility that the catalytic measurements were interfered with the disappearance of acetic acid due to evaporation phenomena during its injection.

Preliminary Results and Discussion

Nitrogen adsorption desorption analyses showed that zirconia samples presented very low surface area (under detection limit of the apparatus, (namely $<20 m^2/g$). In contrast, silica samples presented higher surface area and a little quantity of large micropores and mesopores. Wet impregnated silica showed lower surface area than the support, indicating pore blockage or filling by HPW crystals formation. After washing, the solid recovered the surface area of the support, indicating that HPW is not resistant to leaching in water.

The XRD patterns of zirconia and silica samples showed that the matrix in both cases was amorphous. In the case of solids synthesised by sol-gel method, we obtain a high dispersion of the heteropolyacid as the XRD pattern of pure HPW was absent. However, the solid synthesised by wet impregnation presented a well defined pattern of HPW crystals which disappears after a washing step by Soxhlet extraction. This indicated that the HPW crystals are soluble in water and thus they present a high tendency to leaching in polar media as glycerol. This behaviour is also observed for silica samples as it can be seen in Figure 1.

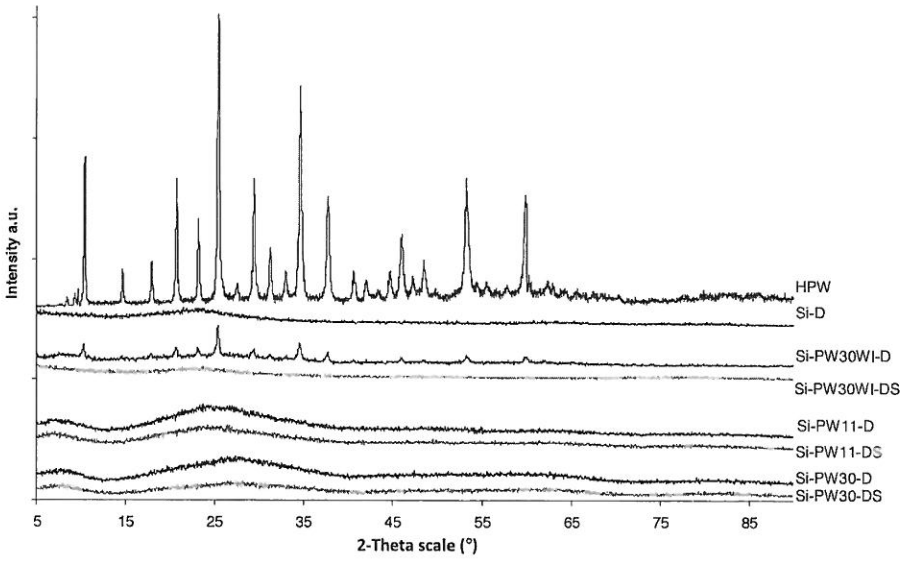

Figure 1. XRD patterns of HPW Immobilised in silica.

The ICP-AES analysis demonstrated that the content of heteropolyacid in the solids synthesised by sol-gel technique remained constant after Soxhlet extraction Moreover it can be seen that zirconia

matrix retains a higher quantity of HPW than silica matrix (Table 1). It can be concluded that sol-gel synthesised solids are resistant to leaching by polar solvents like water, as their extraction with distilled water did not alter their content in HPW.

Table 1. HPW Immobilisation yield by sol-gel method depending on the matrix.

	Immobilisation yield (%)	
Sample	D	DS
Zr-PW30	78,5	81,4
Si-PW11	80,4	81,7
Si-PW30	82,5	44,9

The FTIR spectra of prepared samples exhibited the characteristics bands of the Keggin structure despite the overlapping with the characteristics bands of the matrix. It can be concluded that the Keggin structure is preserved, however some geometric distortions were detected as some positions of the characteristic bands were shifted from the pure HPW spectrum. This phenomenon could be due to a strong interaction between the HPW and the matrix. Moreover, the FTIR spectra of the solids prepared by wet impregnation technique, and washed with distilled water did not exhibit the existence of Keggin HPA units.

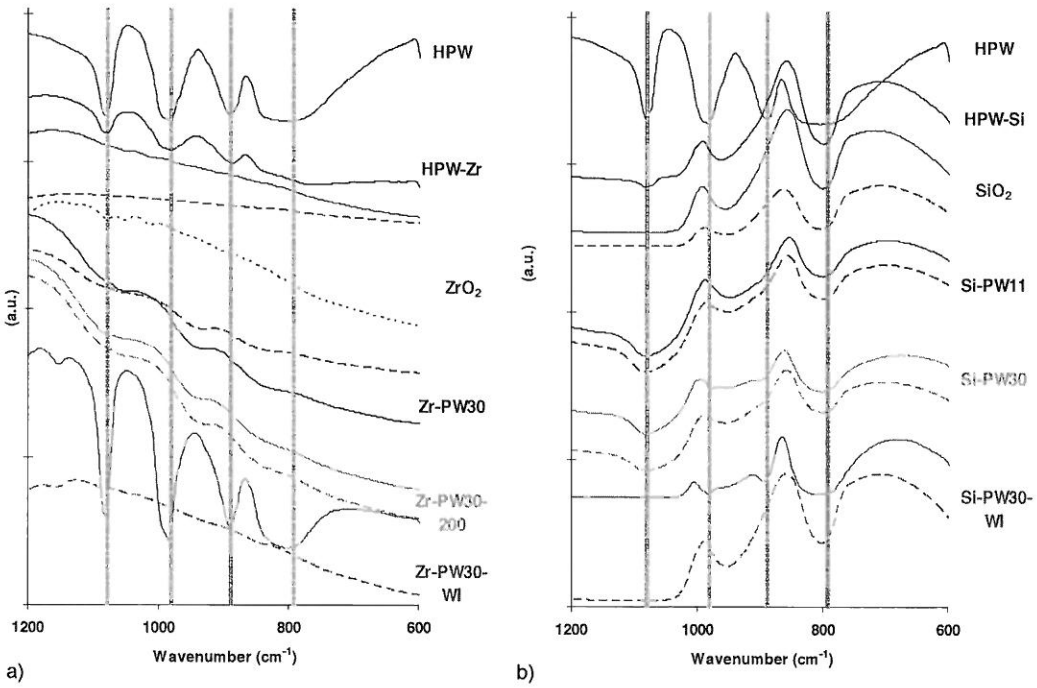

Figure 2. FTIR spectra of HPW immobilised in zirconia (a) and silica matrix (b). Dotted line: after Soxhlet extraction. The vertical lines indicate the FTIR bands corresponding to pure HPW (1080, 981, 890, and 793 cm^{-1}). HPW-Zr and HPW-Si lines represent the expected spectra of a 30%wt HPW solid.

Glycerol acetylation test in homogeneous phase were performed with pure HPA. The mass of HPA used in each reaction is equivalent to the mass of HPA included in a prepared sample with a nominal content of HPA equal to 30%wt. From Figure 3.a) it can be seen that HPW and HSiW exhibit the same acceleration of acetic acid conversion. If this conversion is reported to the quantity of theoretical H^+ loaded in the reaction (Figure 3.b) it can be observed that the acceleration of the reaction is performed

according to the ranking of acidity presented before ($H_3PW_{12}O_{40}$, (HPW)>; $H_4SiW_{12}O_{40}$, (HSiW)> $H_3P_2Mo_{12}O_{40}$ (HPMo) >$H_4SiMo_{12}O_{40}$ (HSiMo)). In addition, working with an equivalent quantity of PMo anion with a NH_4^+ cation, was less active, which shows that protons are absolutely needed to promote the glycerol acetylation.

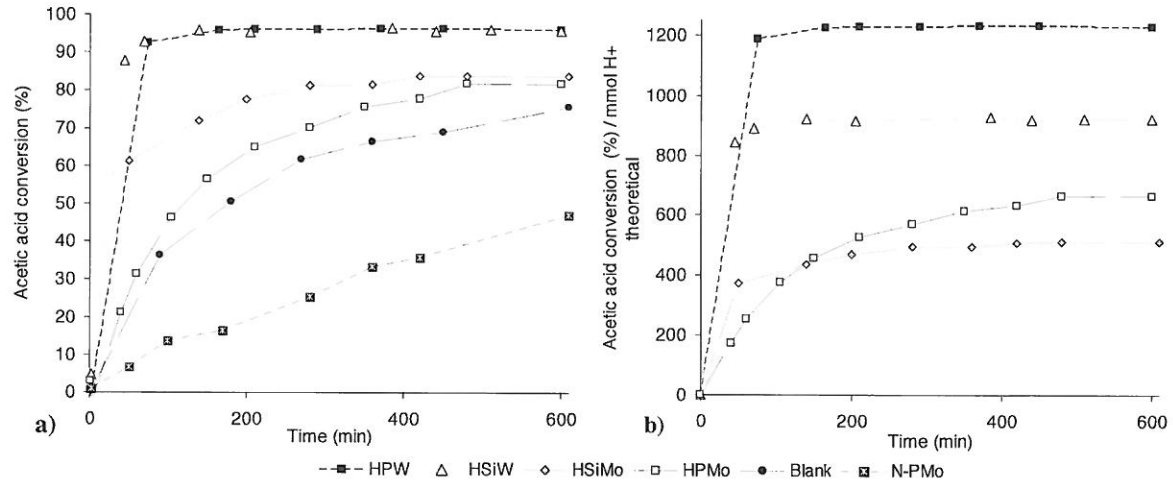

Figure 3. Catalytic performances of pure HPA.

The results concerning the esterification carried out in presence of entrapped or supported HPA are shown in Figure 4. For comparison, the activity of pure HPW is also presented.

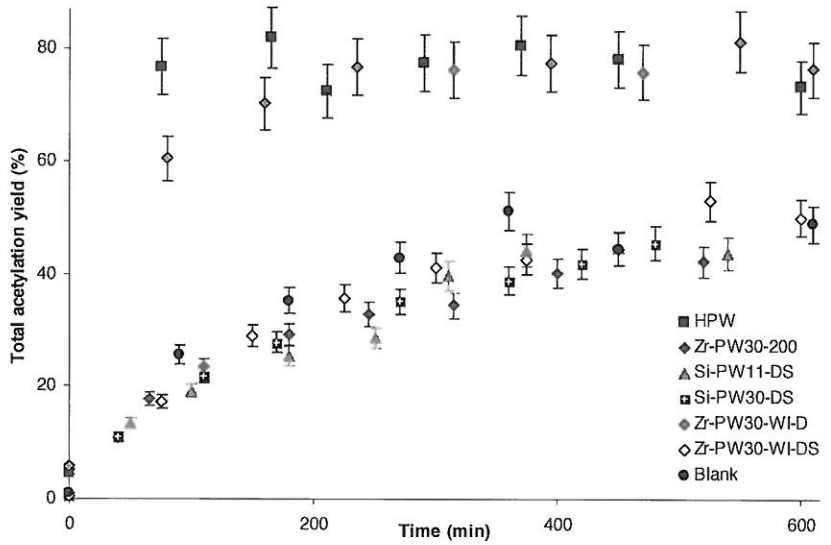

Figure 4. Catalytic performances of HPW immobilised by wet impregnation technique and sol-gel method in zirconia and silica.

It can be observed that HPW immobilised by wet impregnation sample exhibited a catalytic activity very similar to the one obtained for the pure corresponding heteropolyacid. As the same test was performed after Soxhlet extraction it can be seen that the solid did not achieve the same activity. This large difference of activity is due to the leaching of the crystal HPW present in the solid before washing. The leached species act thus as homogeneous catalysts. On the other hand, solids synthesised by sol-gel are inactive in the esterification reaction. This could be related to the lower surface area presented by the

zirconia samples and to the presence of micropores in silica solids, which prevents glycerol access to active sites. In addition, the suspected interaction of Keggin units with the solid matrix could result in a decrease of acidity for the immobilised units compared to the pure heteropolyacids which would thus become inactive in the reaction.

Conclusions

In this work the synthesis and characterisation of HPW incorporated in zirconia and silica by different methods, namely sol-gel and wet impregnation technique, were performed. The properties of the solids were tested in the glycerol acetylation carried out in an excess of glycerol. Zirconia based solids showed very low surface area and silica powders exhibited both micro and mesopores. The structure of the matrix was in all cases amorphous. The sol-gel samples showed a very high dispersion of HPW, contrary to the wet impregnation samples where the presence of HPA crystals was detected. The Keggin HPA unit is maintained in the final powders, even if some geometric distortion was detected by FTIR, probably due to a strong interaction between the HPW and the matrix. The solids synthetized by sol-gel presented a very high resistance to leaching as the HPW content remains constant after extraction with distilled water in Soxhlet apparatus. On the contrary solids prepared by wet impregnation presented a low resistance to leaching.

The HPW immobilised by sol-gel could not accelerate the glycerol acetylation reaction despite the good catalytic performance shown in homogeneous phase. The absence of activity could be explained by the presence of micropores in the solid that prevent the reactants from reaching the active sites. Another reason of this inactivity could also be the modification of acidic properties of HPA when immobilised as they structure is modified due to interactions with the matrix.

Acknowledgements

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